

Tales of the unexpected. The non-random statistical copolymerisation of myrcene and styrene in the presence of a polar modifier.

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Electronic Supporting Information

S1. Experimental

Materials

β -myrcene (≥ 95 %, Sigma Aldrich UK), ReagentPlus styrene (≥ 99 %, Sigma Aldrich UK), TMEDA (≥ 99.5 %, Sigma Aldrich UK), cyclohexane-D₁₂ (≥ 99.6 atom % D, Sigma Aldrich UK) and anhydrous benzene (99.8 %, Sigma Aldrich UK) were dried and degassed, using extra pure calcium hydride (93 %, 0 – 2 mm grain size, Acros Organics) and the freeze-pump-thaw method. *Sec*-butyllithium (*sec*-BuLi) (1.4 M in cyclohexane, Sigma Aldrich UK), laboratory reagent grade propan-2-ol (99.5 %, Fisher Scientific UK), chloroform-D (> 99.8 atom % D, Apollo Scientific Limited) and analytical reagent grade methanol (99.99 %, Fisher Scientific UK) were all used as supplied.

SEC Measurements

Triple detection SEC was carried out using a Viscotek GPC max VE2001 solvent/sample module and a Viscotek Triple Detector Array 302 at 35 °C with a 1 mL min⁻¹ flow rate. A dn/dc value of 0.131 mL g⁻¹ [1] was used for polymyrcene in THF and a dn/dc value of 0.185 mL g⁻¹ was used for polystyrene in THF [2]. A weighted average dn/dc value was calculated for each copolymer based on copolymer composition data obtained by ¹H NMR.

¹H NMR Measurements

¹H NMR spectroscopy was carried out using a Bruker Advance III 400 MHz spectrometer with an operating frequency of 400.130 MHz for ¹H, using deuterated chloroform (CDCl₃) as the solvent. The ¹H NMR kinetic spectroscopy experiment was carried out using a Varian DD2-500 MHz spectrometer with an operating frequency of 499.520 MHz for ¹H, using deuterated cyclohexane (C₆D₁₂) as the solvent.

Differential Scanning Calorimetry

Glass transition temperature analysis was carried out using a Perkin Elmer DSC 8500. Each sample was subjected to a heat-cool-reheat cycle and glass transitions were measured on a reheat cycle, with a heating rate of 100 °C/min.

Polymer Synthesis

PMS1 - 3.21 g (23.6 mmol) of dry, degassed myrcene was mixed with 2.58 g (24.8 mmol) of dry, degassed styrene before being dissolved in approximately 100 mL of dry, degassed benzene. The polymerisation was then initiated with 59 μL (82.7 μmol) of *sec*-BuLi to synthesise a statistical copolymer, with a target M_n of 70,000 g mol⁻¹. The solution was left to stir for 1200 minutes at room temperature before being terminated *via* the injection of an excess of sparged methanol. The polymer was recovered by precipitation into a large excess of methanol, washed and dried in *vacuo* to yield 4.81 g (83 %) of poly(myrcene-*co*-styrene); M_n – 80,700 g mol⁻¹, M_w – 86,800 g mol⁻¹, $\bar{D}$ – 1.08 (as calculated by SEC using a dn/dc value of 0.159); 54.4 % styrene, 45.6 % myrcene (90.3 % (4,1), 9.7 % (4,3)).

PMS(T)1 – was prepared according to the method described above using 4.80 g (35.2 mmol) of myrcene, 3.82 g (36.7 mmol) of styrene and 86 μL (575 μmol) of TMEDA and initiated with 205 μL (287 μmol) of *sec*-BuLi. Yield – 6.38 g (74 %); M_n – 32,600 g mol⁻¹, M_w – 35,300 g mol⁻¹, $\bar{D}$ – 1.08 (as calculated by SEC using a dn/dc value of 0.161); 52.8 % styrene, 47.2 % myrcene (38.1 % (4,1), 57.1 % (4,3), 4.8 % (1,2)).

PMS(T)-NMR - Myrcene (80 μL , 466 μmol) was mixed with styrene (80 μL , 698 μmol), TMEDA (4 μL , 27.2 μmol) and cyclohexane (640 μL) and degassed over CaH₂ before being injected into an NMR tube that had been dried under ultra-high vacuum and then filled with argon. The solution was then initiated with *sec*-BuLi (10 μL , 13.6 μmol), injected *via* syringe, to synthesise a copolymer with a target molecular weight of approximately 10,000 g mol⁻¹, and immediately placed in a NMR machine. The solution was then left for 3 hours at RT, ensuring full monomer conversion, where an NMR spectrum was taken every 150 seconds before the polymerisation was terminated *via* the injection of an excess of sparged isopropanol. PMS(T)-NMR was precipitated into a large excess of isopropanol, washed and dried in *vacuo*. M_n – 15,900 g mol⁻¹, M_w – 17,400 g mol⁻¹, $\bar{D}$ – 1.09 (as calculated by SEC using a dn/dc value of 0.167); 67 % styrene, 33 % myrcene (34 % (4,1), 61 % (4,3), 5 % (1,2)).

S2. Structural Analysis of Poly(myrcene-*stat*-styrene) Copolymers

To calculate the copolymer composition, it is first necessary to calculate the diene microstructure for each copolymer and we must assign each of the peaks in the NMR spectrum of the myrcene-styrene copolymer, with assignments reported in Table S1. The NMR spectrum of PMS1, a statistical copolymer of styrene and myrcene polymerised in benzene is shown in Figure S3 and the NMR spectrum of a statistical copolymer of styrene and myrcene polymerised in benzene in the presence of 2 mole equivalents of TMEDA with respect to BuLi is shown in Figure S4. From the outset it should be noted that there is significant peak overlap between both styrene and myrcene protons and the protons arising from the different diene microstructures.

Table S1: ^1H NMR peak assignments for styrene and the potential microstructures of myrcene. These peak assignments have been made in comparison with assignments of poly(isoprene) [3] and characterisation analysis by Visseaux *et al.* [4] Protons which are unique to 4,3 microstructure are highlighted in red and those unique to 1,2 microstructure are highlighted in blue.

Peak Number	Chemical Shift /ppm	Monomer	Assignment
1	1.25 – 1.70	Styrene and Myrcene	$\text{H}_b + \text{H}_9 + \text{H}_{10} + \text{H}_{4'} + \text{H}_{1''} + \text{H}_{5''}$
2	1.70 – 2.25	Styrene and Myrcene	$\text{H}_a + \text{H}_4 + \text{H}_1 + \text{H}_5 + \text{H}_6 + \text{H}_{3'} + \text{H}_{5'}$
3	4.45 – 4.85	Myrcene	$\text{H}_{1'}$
4	4.85 – 5.20	Myrcene	$\text{H}_3 + \text{H}_7 + \text{H}_{4''}$
5	5.55 – 5.75	Myrcene	$\text{H}_{3''}$
6	6.25 – 6.85	Styrene	H_o
7	6.85 – 7.25	Styrene	$\text{H}_m + \text{H}_p$

The microstructure of PMS1, in keeping with all common dienes is dominated by 4,1-repeat units, with a small contribution of 4,3-units and, as illustrated in Figure S3, no 1,2-repeat units, as evidenced by the absence of a signal at 5.55-5.75 ppm. The 4,1-microstructure can exist as

both *cis* and *trans* units however, in poly(myrcene) the *cis* and *trans* isomers are completely indistinguishable by ^1H NMR spectrometry. [4]

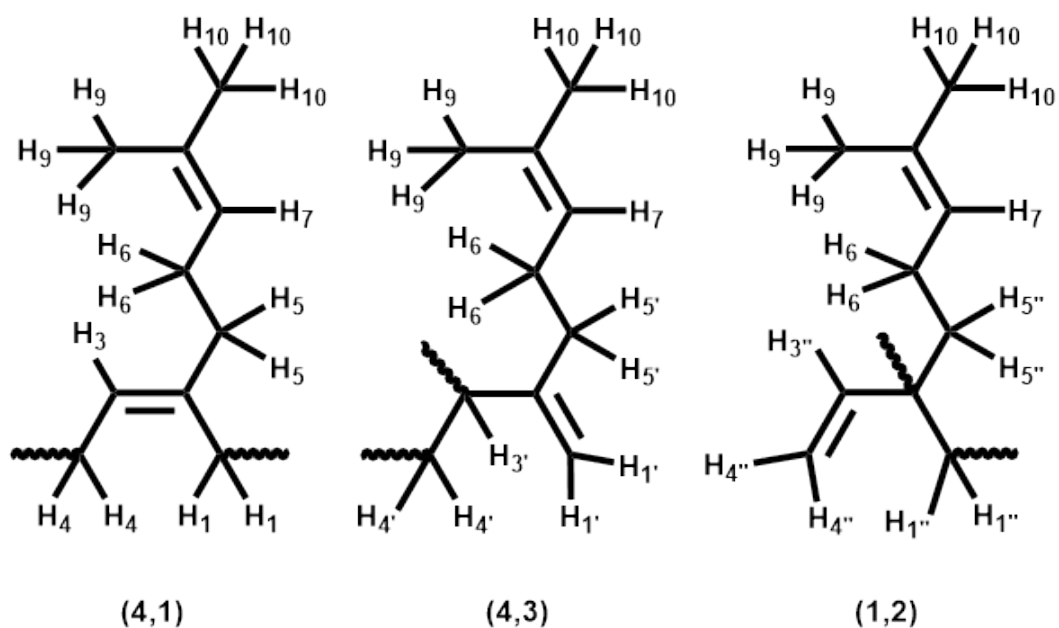


Figure S1: Diagram showing the three possible microstructures of poly(myrcene) with numbered hydrogens for easy assignment.

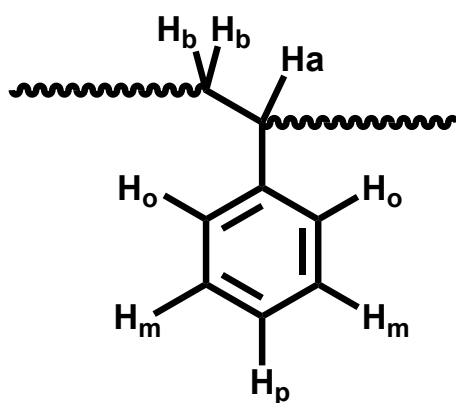


Figure S2: Diagram showing the structure of poly(styrene) with lettered hydrogens for easy assignment.

S2.1 Microstructure of PMS1

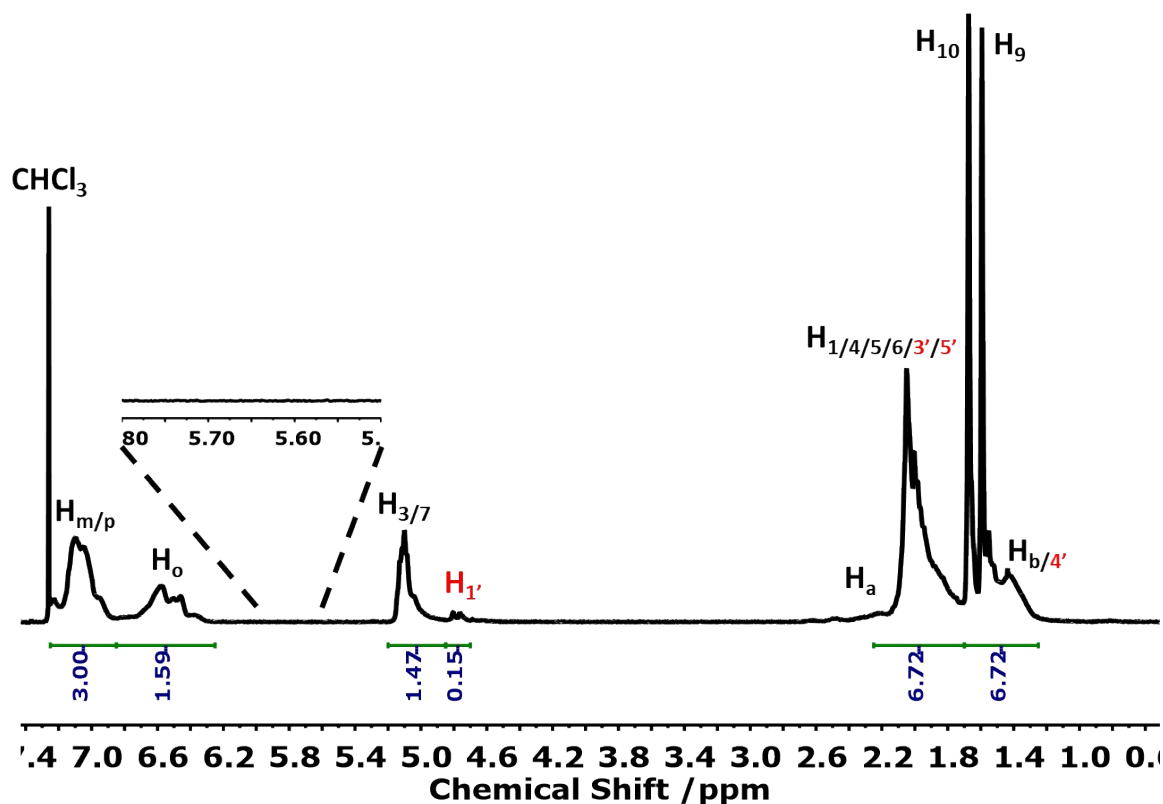


Figure S3: ^1H NMR spectrum of PMS1 with hydrogen assignment of each of the peaks.

To calculate the microstructure of PMS1 we can use;

- Peak 4 (4.85-5.20 ppm), which corresponds to 2 protons from 4,1 repeat unit (**H₃** and **H₇**) overlapped with 1 proton from 4,3 repeat units (again **H₇** – which is common to all microstructures) and
- Peak 3 (4.70-4.85 ppm), which corresponds to 2 protons from the 4,3 repeat unit (**H_{1'}**).

Thus the % 4,1 microstructure is given by equation S1:

Equation S1

% 4,1 microstructure =

$$\frac{Integral\ Peak\ 4 - \left(\frac{Integral\ Peak\ 3}{2}\right)}{Integral\ Peak\ 4 - \left(\frac{Integral\ Peak\ 3}{2}\right) + Integral\ Peak\ 3} \times 100$$

Using the integrals for PMS1 in Figure S2 we get

$$\% \text{ 4,1 microstructure} = \frac{1.47 - \left(\frac{0.15}{2}\right)}{1.47 - \left(\frac{0.15}{2}\right) + 0.15} \times 100 = 90.3 \%$$

$$\% \text{ 4,3 microstructure} = 100 \% - 90.3 \% = 9.7 \%$$

S2.2 Microstructure of PMS(T)1

The addition of TMEDA to the copolymerisation (PMS(T)1) is expected to significantly impact the diene microstructure and lead to a lower fraction of 4,1, a significantly higher fraction of 4,3 and the introduction of a small fraction of 1,2 repeat units – as evidenced by the presence of a small peak in the region between 5.55 – 5.75 ppm, which arises due to the presence of protons H₃'' in the NMR spectrum of PMS(T)1 (Figure S4). However, the microstructure of PMS(T)1 can be calculated using the integrals of peaks 3, 4 and 5 where;

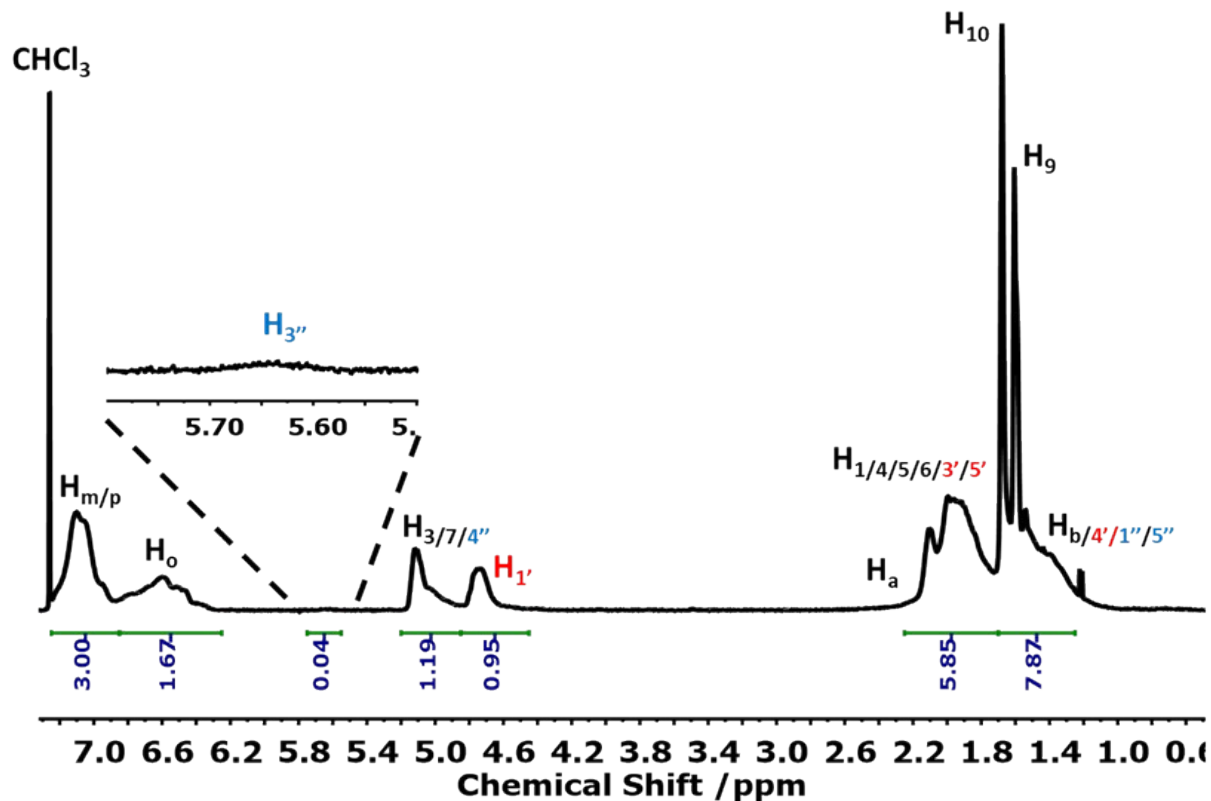


Figure S4: ^1H NMR spectrum of PMS(T)1 with hydrogen assignment of each of the peaks.

- Peak 3 (4.45-4.85 ppm), which corresponds to 2 protons from 4,3 repeat units ($\text{H}_{1'}$)
- Peak 4 (4.85-5.20 ppm), which corresponds to 2 protons from 4,1 repeat units (H_3 and H_7) and 1 proton from 4,3 repeat units (again H_7 – which is common to all microstructures) and
- Peak 5 (5.55-5.75 ppm), which corresponds to 1 proton from 1,2 repeat units ($\text{H}_{3''}$)

Thus the integral equivalent to 2 protons from 4,1 repeat units is given by Equation S2;

Equation S2

$$2H_{4,1} = \text{Integral Peak 4} - \frac{\text{Integral Peak 3}}{2} - (2 \times \text{Integral Peak 5})$$

$$2H_{4,1} = 1.19 - \frac{0.95}{2} - (2 \times 0.04) = 0.635$$

The integral equivalent to 2 protons from 4,3 repeat units is equal to the integral of Peak 3 (0.95) and the integral equivalent to 2 protons from 1,2 repeat units is given by 2 x the integral

of Peak 5 (0.08). These values can be used to calculate the % 4,1-, % 4,3- and % 1,2-units using equations S3, S4 and S5 respectively.

$$\text{Equation S3} \quad \% 4,1 \text{ microstructure} = \frac{0.635}{0.635 + 0.95 + 0.08} \times 100 = 38.1\%$$

$$\text{Equation S4} \quad \% 4,3 \text{ microstructure} = \frac{0.95}{0.635 + 0.95 + 0.08} \times 100 = 57.1 \%$$

$$\text{Equation S5} \quad \% 1,2 \text{ microstructure} = \frac{0.08}{0.635 + 0.95 + 0.08} \times 100 = 4.8 \%$$

S2.3 Compositional Analysis of Poly(myrcene-*stat*-styrene) Copolymers

Knowing the make-up of the microstructure of the diene units, it is possible to calculate the molar composition (myrcene : styrene) of the copolymer.

S2.3.1 Compositional analysis of PMS1

Using the peak integrals in the NMR spectrum of PMS1 (Figure S3) and discussion above, we know that the integral value of 2H for the 4,1 microstructure is given by Equation S6 below;

$$\text{Equation S6} \quad 2H_{4,1} = \text{Integral Peak 4} - \left(\frac{\text{Integral Peak 3}}{2} \right) = 1.47 - \left(\frac{0.15}{2} \right) = 1.395$$

As PMS1 is 90.3 % 4,1 repeat units the integral value for 2H for all microstructures = 1.54

The sum of the integral values of peaks 6 and 7 (Table S1 and Figure S3) arise due to the 5 ring protons of styrene repeat units. Thus, the integral value for 2H_{sty} is given by Equation S7;

$$\text{Equation S7} \quad \frac{2H_{sty}}{2 \times (\text{Integral Peak 6} + \text{Integral Peak 7})} = \frac{2 \times (1.59 + 3.00)}{5} = 1.836$$

$$1.84$$

Thus, the mole fraction of styrene in PMS1 = $\frac{1.84}{1.84 + 1.54} = 0.544$

The mole fraction of myrcene in PMS1 = 1 – 0.544 = 0.456.

The molar compositions of PMS1 samples collected at intermediate times were calculated in the same way.

S2.3.2 Compositional analysis of PMS(T)1

Using the peak integrals in the NMR spectrum of PMS(T)1 (Figure S4) and discussion above, we know that the integral value (0.635) of 2H for the 4,1 microstructure is given by Equation S2 above, and PMS(T)1 comprises 38.1% 4,1 repeat units. Using these data, the sum of the integrals for peaks 6 and 7 (1.67 and 3.00 respectively) and the approach described above we calculate the mole fraction of styrene in PMS(T)1 equals 0.528 and the mole fraction of myrcene 0.472.

Table S2: The comonomer composition and myrcene microstructure for PMS1 and PMS(T)1.

Copolymer	Styrene in the copolymer /%	Myrcene composition /%		
		(4,1)	(4,3)	(1,2)
PMS1	54.4	90.3	9.7	0.0
PMS(T)1	52.8	38.1	57.1	4.8

S3. ¹H NMR Spectroscopy “Blockiness” Calculation

¹H NMR data can also be used to determine the “blockiness” of styrene in styrene-diene copolymers. This approach attempts to determine the proportion of styrene units that appear next to another styrene unit but is generally only valid when 3 or 4 or more styrene units are adjacent in a block. This approach uses NMR signals from the styrenic aromatic protons and specifically the chemical shift of the ortho protons, which is highly sensitive to the nature of adjacent monomer units. Thus when a styrene unit is found in a block of three or more styrene molecules, the ortho signal is found at 6.25 - 6.85 ppm (defined herein as Peak [B]) and the para/meta signals are found at 6.85 - 7.25 ppm (defined herein as Peak [A]). See Figures S5 and S6 which show the ¹H NMR spectra of a polystyrene and poly(myrcene-*block*-styrene).

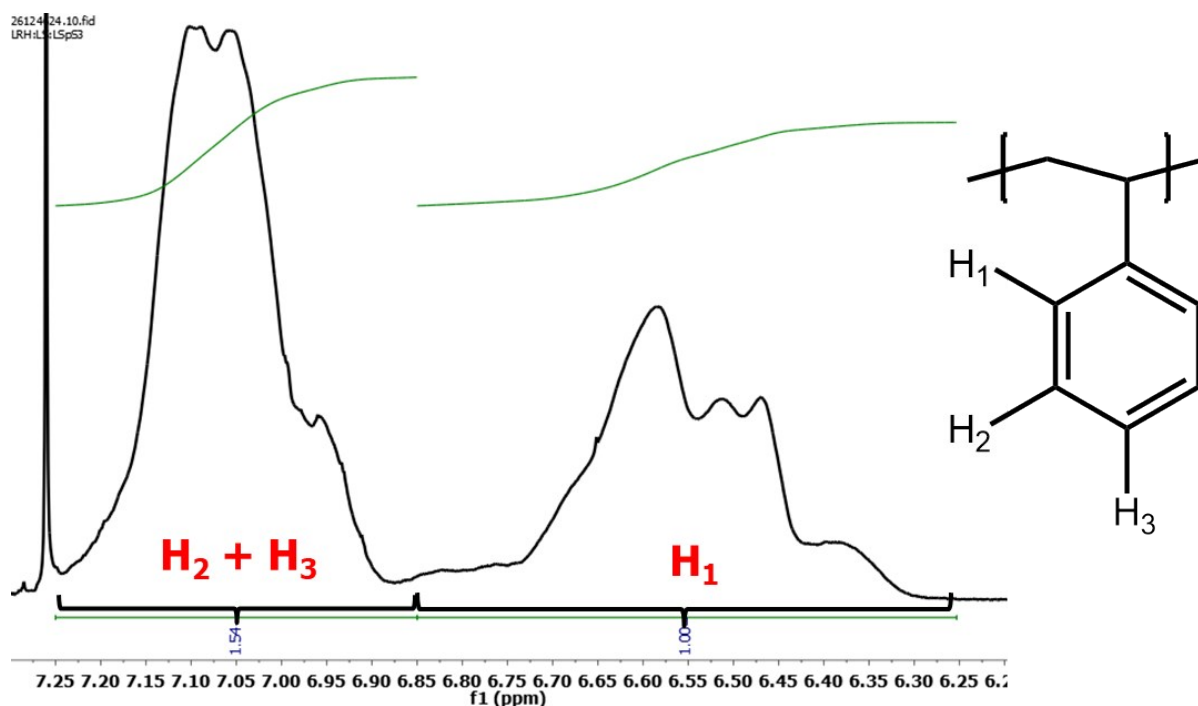


Figure S5. ¹H-NMR of polystyrene homopolymer indicating chemical shifts of ortho (H₁), meta (H₂) and para (H₃) protons of polystyrene.

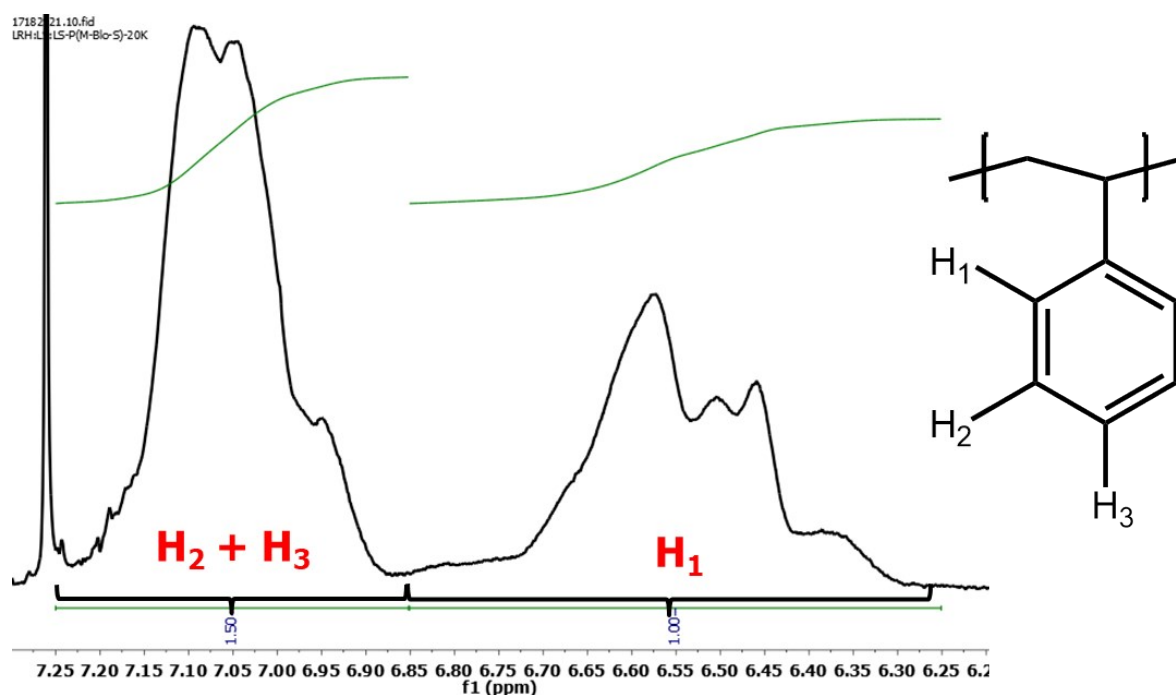


Figure S6. ¹H-NMR of poly(myrcene-*block*-styrene) indicating chemical shifts of ortho (H₁), meta (H₂) and para (H₃) protons of polystyrene block.

However, when a styrene unit is not found in a block of three styrene molecules, as would be expected for a random styrene-diene copolymer, the ortho proton signal is shifted down-field so that the peak is found in the same region as the meta and para signals (see Figure S7) –

note that in Figure S7 chemical shift is measured in τ rather than ppm and thus the ortho proton signal appears at 3.5 τ and the meta/para signals at 3.0 τ .

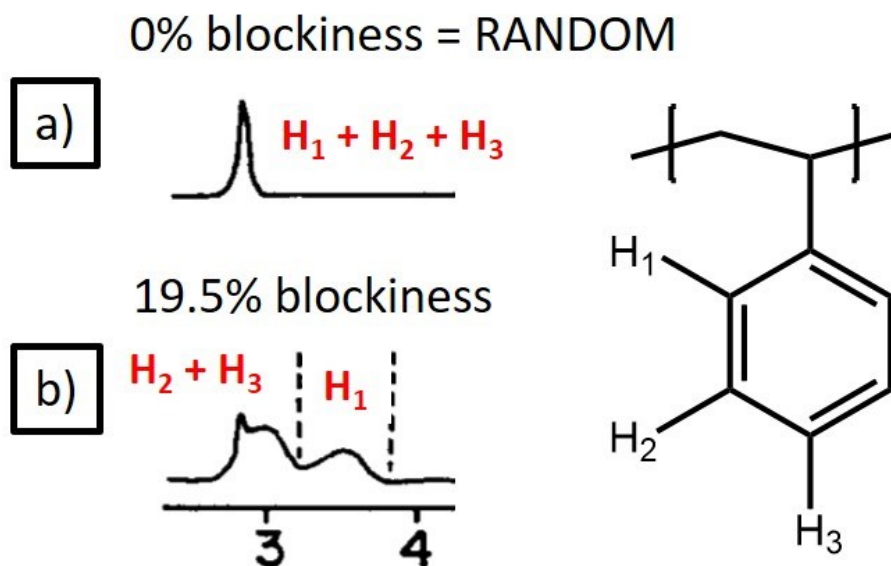


Figure S7. ^1H -NMR spectra of butadiene-styrene copolymers with varying composition and degree of blockiness a) 17 % styrene, 0 % blockiness (i.e. random); b) 28 % styrene, 19.5 % blockiness. Figure modified version of figure 3 ref [5].

Based on this observation, an equation to calculate the “randomness/blockiness” of styrene has been devised, [6] (Equation S8 and S9) but what these calculations actually define is the proportion of styrene units that are found in a block of three or more styrene units.

Equation S8 “Randomness” percentage =
$$\frac{[A] - 1.5[B]}{[A] + [B]} \times 100 \%$$

Equation S9 “Blockiness” percentage = $100 - \text{“Randomness” Percentage}$

To demonstrate that the myrcene-styrene copolymers PMS1 and PMS(T)1 are both block-like the percentage “blockiness” of each was calculated using NMR data from the spectra in Figures S8 and S9.

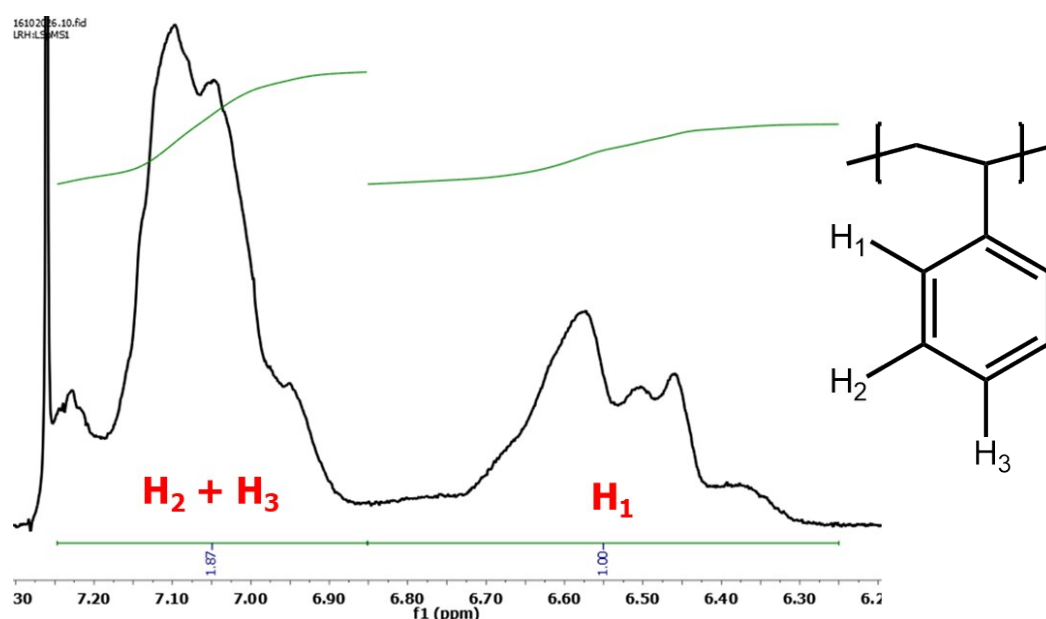


Figure S8. ^1H -NMR of PMS1 (poly(myrcene-*stat*-styrene) - no TMEDA) indicating chemical shifts of ortho (H_1), meta (H_2) and para (H_3) protons of styrene repeat units.

PMS1 has a molar ratio of 54.4 % styrene and 45.6 % myrcene with a M_n of 80,700 g mol^{-1} . Ratio of Peak [A] to Peak [B] = 1.87 : 1 therefore degree of randomness = $(0.37/2.87) \times 100 = 12.89\%$. Thus c. 87 % of the styrene units are found in a block of 3 or more styrene units.

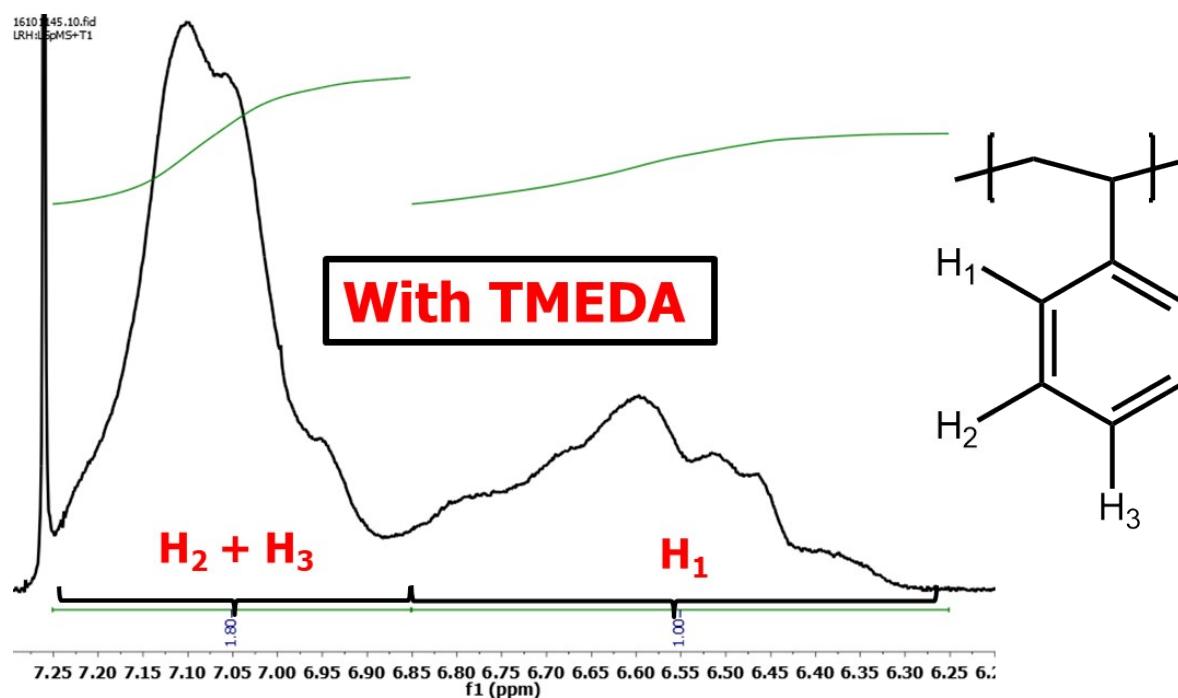


Figure S9. ^1H -NMR of PMS(T)1 (poly(myrcene-*stat*-styrene) – with TMEDA) indicating chemical shifts of ortho (H_1), meta (H_2) and para (H_3) protons of styrene repeat units.

PMS(T)1 has a molar ratio of 52.8 % styrene and 47.2 % myrcene with M_n of 32,600 g mol^{-1} .

Ratio of Peak [A] to Peak [B] = 1.8 : 1 therefore degree of randomness = $(0.3/2.8)*100 = 10.71\%$. Thus 89 % of the styrene units are found in a block of 3 or more styrene units.

S4. Real-time *In-Situ* ^1H NMR Spectroscopy

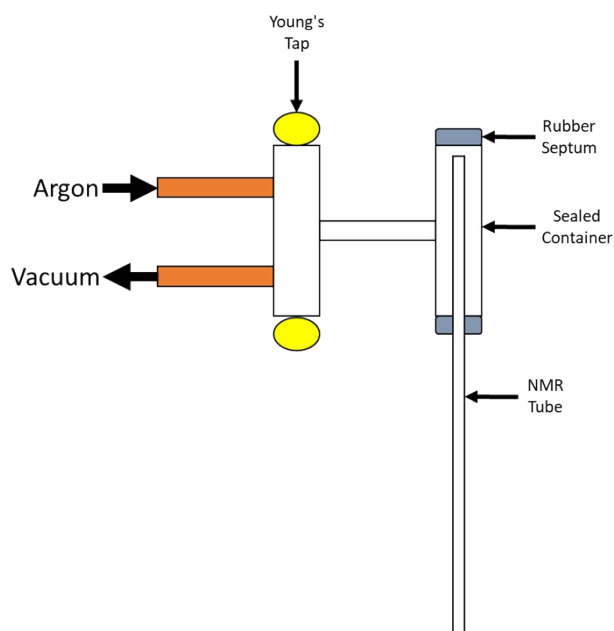


Figure S10: Schematic of equipment used to prepare the NMR tube for LAP.

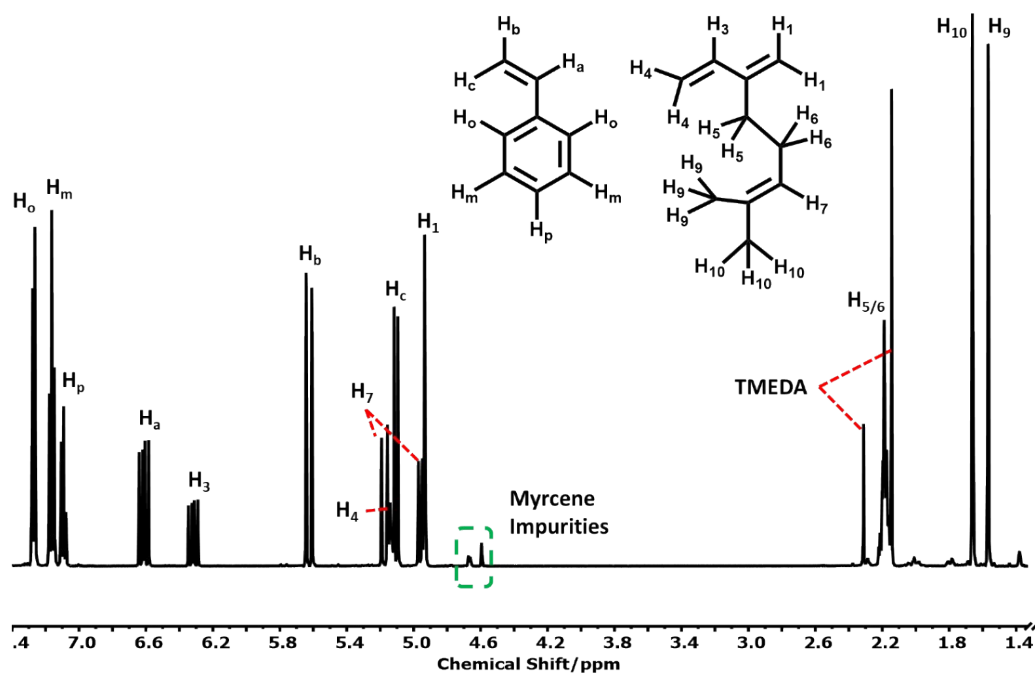


Figure S11: ^1H NMR spectrum of monomer feed for PMS(T)-NMR, with hydrogen assignment of each of the peaks, prior to initiation with BuLi.

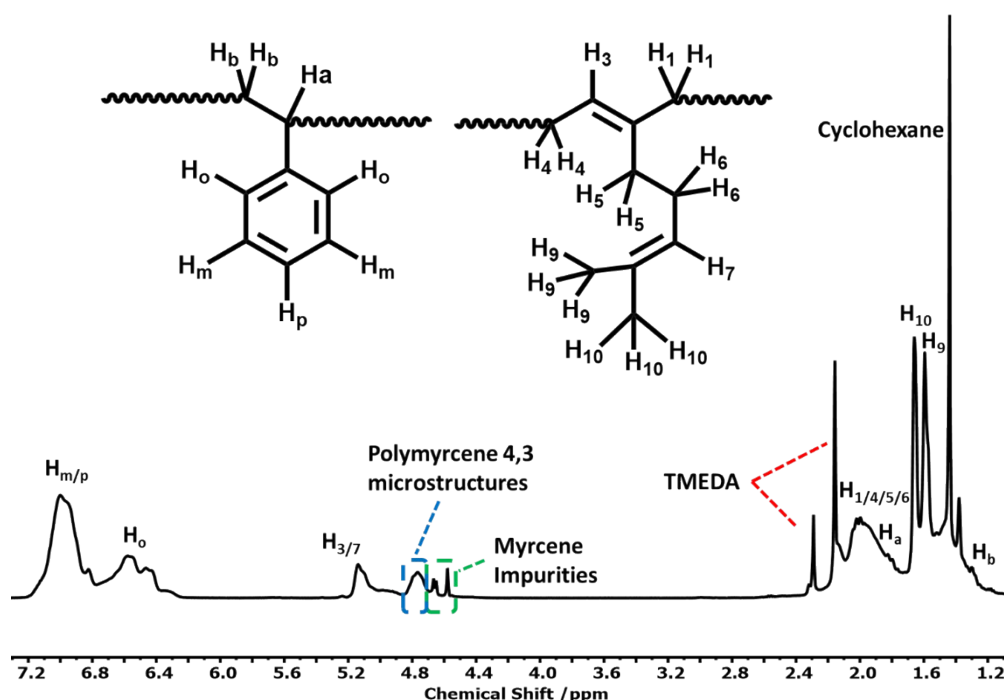


Figure S12: ¹H NMR spectrum of PMS(T)-NMR, with hydrogen assignment of each of the peaks, after polymerisation has occurred.

S4.1 Real-time *In-Situ* ¹H NMR Spectroscopy – Correction Calculation

As mentioned in the main text of the manuscript, a potential error arises in the calculation used to generate the data presented in Figure 3. Specifically, the peak for the myrcene monomer proton H₁ at 6.27-6.37 ppm, which was used to calculate myrcene monomer depletion, overlaps with the emerging peak for the ortho phenyl protons of polystyrene. This is illustrated in Figure S13. This introduces a potential error and a correction was made in an attempt to rectify the error. Thus, the magnitude of the integral for the specific portion of the peak arising from the ortho aromatic proton (6.27-6.37 ppm) which overlaps with the myrcene monomer proton H₃ at 6.27-6.37 ppm was estimated, for each NMR integral that was used. Figure S14 shows the final NMR from the series of stacked spectra in Figure 2 and in this case, there is no overlap because there is no unreacted myrcene monomer and 100 % of the styrene has reacted. We estimated the integral of the portion which would overlap in this case (0.73) and then scaled the integral as a function of styrene conversion. Thus, the assumption is that if the integral value of the overlapping portion at 100 % styrene conversion is 0.73, then at 57 % styrene conversion the integral value of the overlapping portion will be 0.73 x 0.57 which equals 0.416.

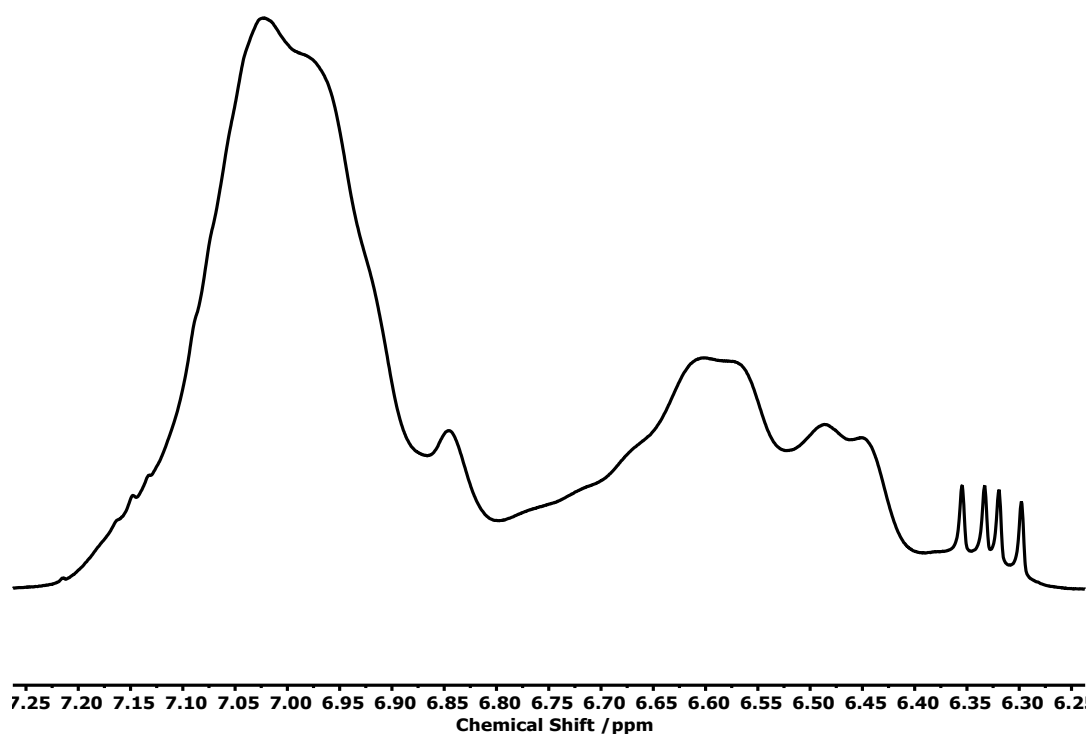


Figure S13: ^1H NMR spectrum of PMS(T)-NMR showing the styrenic region as the polymerisation is progressing, illustrating that the polystyrene ortho proton peak (6.8 – 6.25 ppm) overlaps with the myrcene monomer peak at 6.27 – 6.37 ppm.

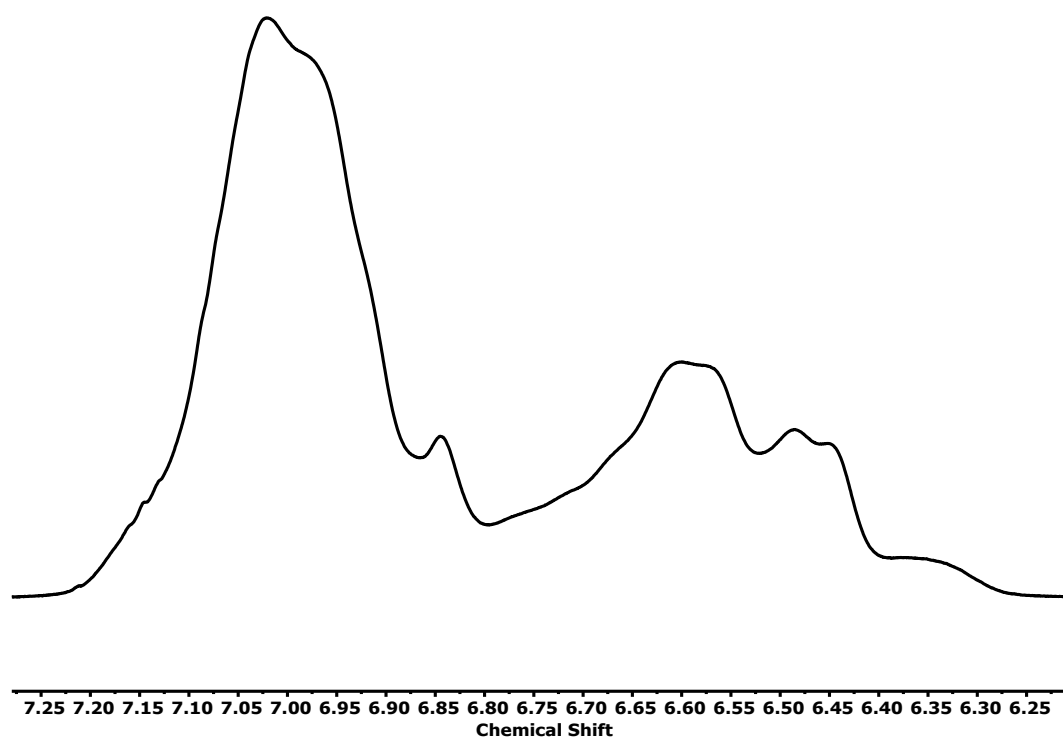


Figure S14: ^1H NMR spectrum of PMS(T)-NMR showing the styrenic region after the polymerisation has occurred to show the magnitude of the peak that overlaps with the myrcene monomer peak.

S4.2 Real-time *In-Situ* ¹H NMR Spectroscopy – Reactivity Ratio Calculation

In-situ, real-time NMR spectroscopy allows the calculation of instantaneous monomer feed ratio data and total (combined) monomer conversion, by monitoring monomer depletion. To reduce any error arising from the impact of a non-zero integral value due to baseline noise, a baseline subtraction was applied to the integral values used for the calculation of the reactivity ratios. Thus integral data was “normalised” such that the regions of the spectrum where the monomer peaks (would) appear in the final NMR spectrum in the series, where no residual monomer is present, are given an total integral value of zero.

Thus using experimental instantaneous monomer feed ratio data from NMR, and the Meyer-Lowry equation (Equation S10), reactivity ratios were estimated for the statistical copolymerisation of styrene and myrcene, in a non-polar solvent, in the presence of TMEDA.

$$Conv = 1 - \left(\frac{f_A}{f_A^0} \right)^{r_B / (1 - r_B)} \left(\frac{1 - f_A}{1 - f_A^0} \right)^{r_A / (1 - r_A)} \times \left(\frac{f_A(2 - r_A - r_B) - r_B - 1}{f_A^0(2 - r_A - r_B) - r_B - 1} \right)^{(r_A r_B - 1) / ((1 - r_A)(1 - r_B))}$$

Equation S10: Meyer-Lowry equation which was used for determining the reactivity ratios of the copolymerisation where f_A is the instantaneous feed ratio of monomer A, f_A^0 is the initial monomer feed ratio of A, r_A is the reactivity ratio of monomer A and r_B is the reactivity ratio of monomer B. [7]

The Meyer-Lowry (M-L) approach allows data at all monomer conversions to be used, rather than just data at low (< 5%) conversion, as required by widely-used linear estimation methods such as the Fineman–Ross [8] and Kelen–Tüdös [9] methods. [10] [11] Moreover, such linear methods have been shown to lack statistical rigour for all systems. The M-L approach also means that data from a single copolymerisation reaction can be used to estimate reactivity ratios, rather than needing to repeat the copolymerisation using several different feed ratios. The (experimental) instantaneous monomer feed ratios obtained by NMR and assumed reactivity ratios are used to estimate a (calculated) total monomer conversion and the process iterated to minimise the difference between the calculated and experimental monomer conversion. Reactivity ratios of $r_{Sty} = 16.67$ and $r_{Myr} = 0.14$ were obtained. A plot of i) the experimental monomer conversion from NMR data and ii) conversion calculated using the estimated reactivity ratios versus f_A – the mole fraction of styrene in the instantaneous feed ratio is shown in Figure S15 below. The agreement between experimental and calculated

conversion data is extremely good, indicating a good fit with an R^2 value of 0.991806. However,

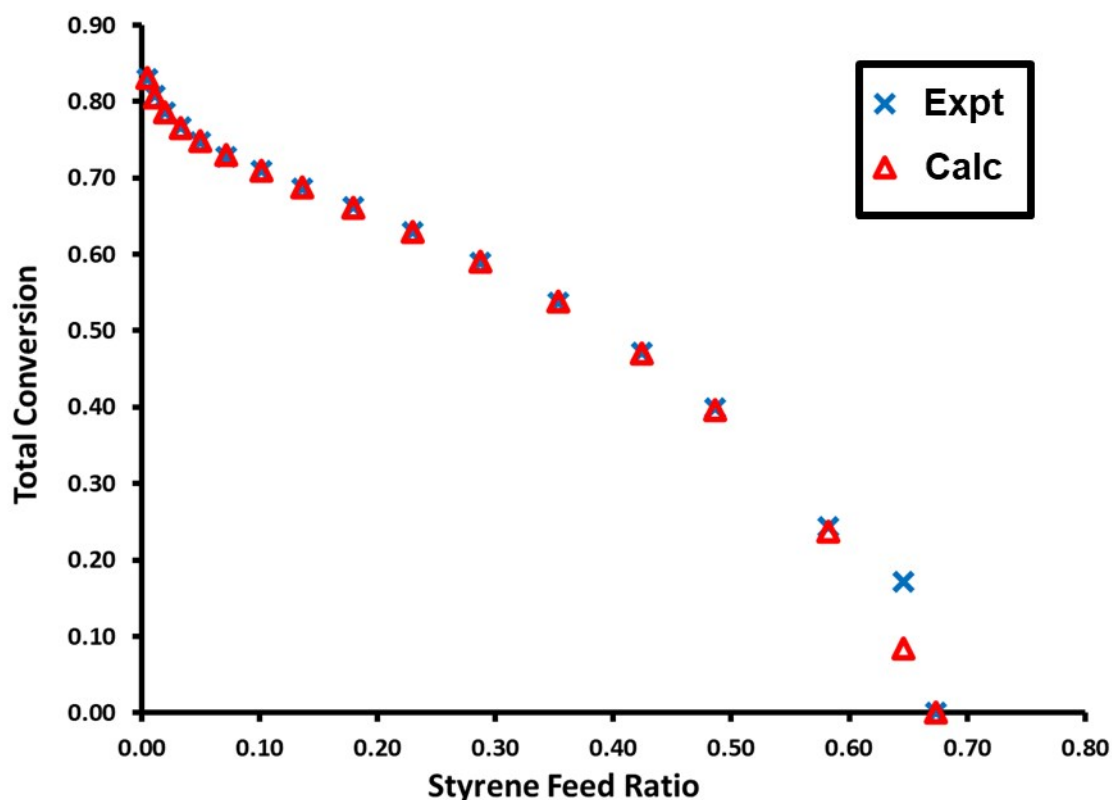


Figure S15: Graph illustrating the experimental total monomer conversion (blue crosses) and monomer conversion calculated using estimated reactivity ratios (red triangles) at varying values of mole fraction styrene in instantaneous monomer feed ratio.

it is worth noting that there is a significant discrepancy between the experimental and calculated total monomer conversion for the first set of NMR data where the fraction of styrene in the instantaneous feed has reduced to 0.65. Thus, whilst experimental conversion based on raw NMR data is c. 18%, the conversion value calculated using the estimated reactivity ratios is a little less than 10%. The source of this discrepancy could be experimental or analytical and which, is not immediately obvious. However, the significant difference between experimental and calculated does impact on the iteration process, which seeks to minimise differences, and the reactivity ratios obtained. The process of estimating reactivity ratios was therefore repeated, whilst excluding the aforementioned data, giving values of $r_{\text{sty}} = 17.52$ and $r_{\text{Myr}} = 0.15$. The agreement between experimental and calculated monomer

conversion was extremely good, indicating an improved (excellent) fit with an R^2 value of 0.999908.

S5. Differential Scanning Calorimetry

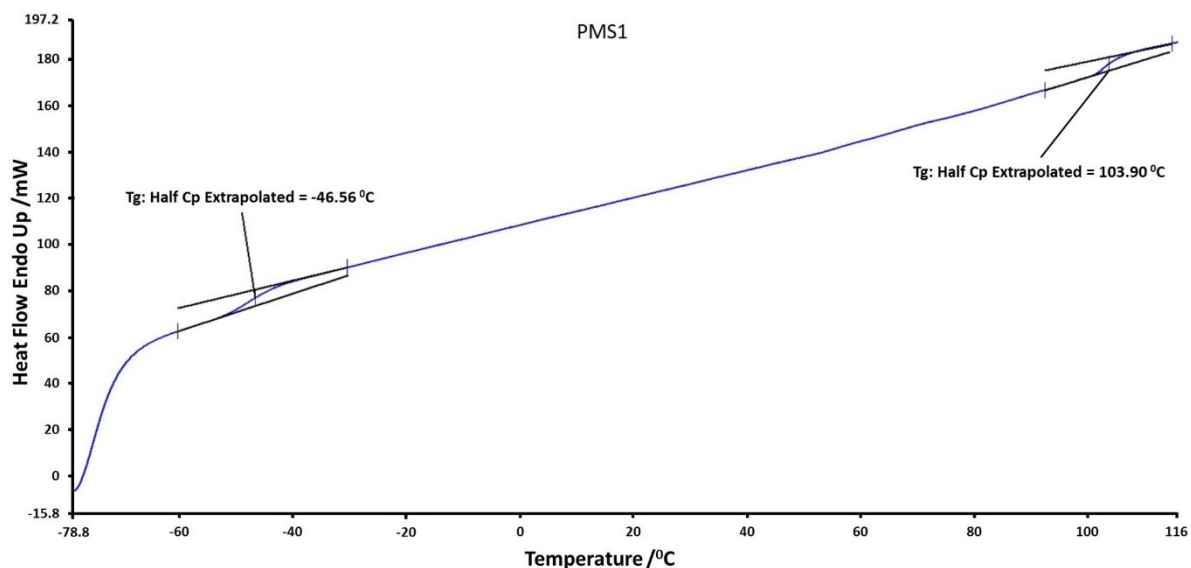


Figure S16: DSC thermogram of PMS1

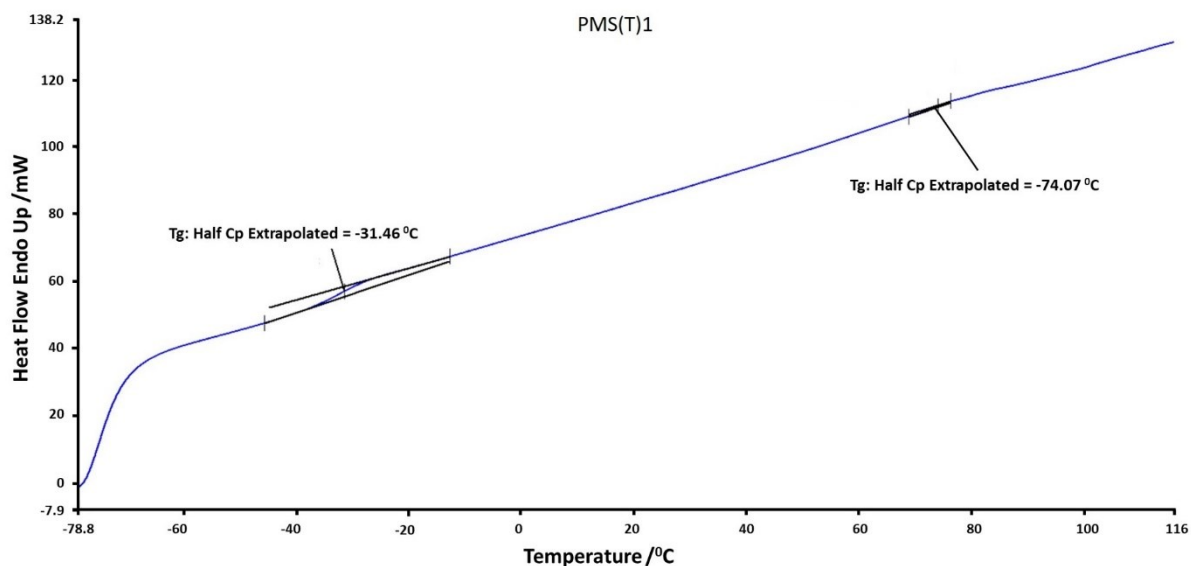


Figure S17: DSC thermogram of PMS(T)1

S6. References

- [1] R. P. Quirk and T.-L. Huang, "Alyllithium-Initiated Polymerization of Myrcene," in *New Monomers and Polymers*, New York, Springer US, 1984, pp. 329-355.
- [2] L. R. Hutchings, P. P. Brooks, D. Parker, J. A. Mosely and S. Sevinc, "Monomer Sequence Control

via Living Anionic Copolymerization: Synthesis of Alternating, Statistical, and Telechelic Copolymers and Sequence Analysis by MALDI ToF Mass Spectrometry," *Macromolecules*, vol. 48, no. 3, pp. 610-628, 2015.

- [3] J. Geng, Y. Sun and J. Hua, "1,2- and 3,4-Rich Polyisoprene Synthesized by Mo(VI)-Based Catalyst with Phosphorus Ligand," *Polymer Science, Series B*, vol. 58, no. 5, pp. 495-502, 2016.
- [4] S. Georges, M. Bria, P. Zinck and M. Visseaux, "Polymyrcene microstructure revisited from precise high-field nuclear magnetic resonance analysis," *Polymer*, vol. 55, pp. 3869-3878, 2014.
- [5] V. D. Mochel, "NMR Composition Analysis of Copolymers," in *Rubber Chemistry and Technology*, Montreal, Canada, 1967.
- [6] A. F. Halasa, C. Jusinas, W.-L. Hsu and D. J. Zanzig, "Random low vinyl styrene-isoprene copolymers," *European Polymer Journal*, vol. 46, pp. 2013-2018, 2010.
- [7] V. E. Meyer and G. G. Lowry, "Integral and Differential Binary Copolymerization Equations," *Journal of Polymer Science: Part A*, vol. 3, pp. 2843-2851, 1965.
- [8] M. Fineman and S. D. Ross, "Linear Method for Determining Monomer Reactivity Ratios in Copolymerization," *Journal of Polymer Science*, vol. 5, no. 2, pp. 259-265, 1949.
- [9] T. Kelen and F. Tudos, "Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios A New Improved Linear Graphic Method," *Journal of Macromolecular Science: Part A - Pure and Applied Chemistry*, vol. 9, no. 1, pp. 1-27, 1975.
- [10] N. A. Lynd, R. C. Ferrier Jr. and B. S. Beckingham, "Recommendation for Accurate Experimental Determination of Reactivity Ratios in Chain Copolymerization," *Macromolecules*, vol. 52, pp. 2277-2285, 2019.
- [11] E. Grune, J. Bareuther, J. Blankenburg, M. Appold, L. Shaw, A. H. E. Muller, G. Floudas, L. R. Hutchings and H. Frey, "Towards bio-based tapered block copolymers: the behaviour of myrcene in the statistical anionic copolymerisation," *Polymer Chemistry*, vol. 10, pp. 1213-1220, 2019.